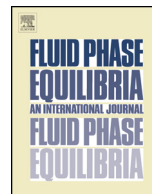




Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid



Single-ion hydration thermodynamics from clusters to bulk solutions: Recent insights from molecular modeling[☆]

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ARTICLE INFO

Article history:

Received 21 March 2015
Received in revised form 28 May 2015
Accepted 30 May 2015
Available online xxx

Keywords:

Single-ion hydration
Molecular modeling
Extrathermodynamic assumption
Cluster ion
Surface potential

ABSTRACT

The importance of single-ion hydration thermodynamic properties for understanding the driving forces of aqueous electrolyte processes, along with the impossibility of their direct experimental measurement, have prompted a large number of experimental, theoretical, and computational studies aimed at separating the cation and anion contributions. Here we provide an overview of historical approaches based on extrathermodynamic assumptions and more recent computational studies of single-ion hydration in order to evaluate the approximations involved in these methods, quantify their accuracy, reliability, and limitations in the light of the latest developments. We also offer new insights into the factors that influence the accuracy of ion–water interaction models and our views on possible ways to fill this substantial knowledge gap in aqueous physical chemistry.

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1. Introduction

The relative magnitude of cation and anion contributions to hydration thermodynamics and local charge imbalances are the main driving forces behind physical and chemical processes in inhomogeneous electrolytes, which are responsible for the formation of the electric double layer at interfaces, selective ion adsorption and separation, diffusion through solutions and membranes, protein denaturation, or transport through ion channels in biological systems.

The importance of the subject and impossibility [1–3] of direct experimental measurement of single-ion thermodynamics in bulk solutions has motivated development of a multitude of approximate approaches intended to overcome the limitations given by the electroneutrality condition. These so-called extrathermodynamic assumptions (ETA) are based on physically motivated

intuitive ideas about ion–water interactions, typically involving some form of assumed symmetry to split neutral salt properties to cation and anion contributions, but different assumptions result in significantly different predictions [4–9]. The estimated Gibbs free energies and enthalpies of hydration from various ETAs are spread over the range of 40–50 kJ/mol, *i.e.*, the energy corresponding to two typical hydrogen bonds, and could result in qualitatively different solvation structures. Moreover, some of these estimated values are still used to develop molecular models of ion–water interactions [10] or form a part of *ab initio* computational techniques [11,12], so the potential errors can affect computer simulations and propagate to other studies.

A more promising way to determine single-ion hydration thermodynamics is based on molecular-scale understanding of ion–water interactions derived from first principles [13]. Ultimately, this bottom–up approach would be based on quantum chemical calculations, and with a perfect representation of interparticle interactions and large computational resources, this method will, in principle, arrive at the correct values. However, the current limitations on the size of the investigated system require the use of approximative techniques that may introduce uncertainties of their own. These size and time restrictions on the simulated system can be overcome with molecular simulations using effective classical force fields, whose speed makes it possible to study large-scale bulk solutions and interfacial systems needed to capture reliably the effects of the surface potential. The critical part of molecular modeling is the adequacy and accuracy of the used force fields, which should be comparable to high-level *ab initio*-predicted interactions and thoroughly validated against

[☆] This manuscript has been authored by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a non-exclusive, paidup, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes. The Department of Energy will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (<http://energy.gov/downloads/doe-public-access-plan>).

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<http://dx.doi.org/10.1016/j.fluid.2015.05.048>

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reliable experimental data. It follows that careful evaluation of experimental reference data, use of high-level quantum chemical methods, and various consistency checks are a prerequisite for accurate representations of ion–water interactions and reliable predictions of single-ion hydration thermodynamics.

In this article we evaluate the current approaches used to investigate ion hydration and include recent insights into the factors that adversely influence the accuracy of the ETAs, quantum chemical methods, and classical molecular force fields. We also suggest ways to either minimize these factors or correct their effect in order to achieve the related goals of accurate description of ion–water interactions and single-ion hydration thermodynamics. For simplicity, we restrict the discussion to systems in which ions only interact with water without interference from other species, such as in infinitely diluted solutions or in gas-phase clusters. Since the separation of cation and anion contributions can be done for any ion pair while the rest can be computed from known neutral salt values, we focus on simple atomic ions that do not exhibit complex behavior, e.g., vibrational, rotational, and electronic degrees of freedom of molecular ions that may preclude stability in the gas phase [14]. This scenario corresponds to the typical subject of other computational studies, in which quantum chemical methods often concentrate on the hydration of H^+ and OH^- ions, as they are light and can be treated at the same level as the surrounding H_2O molecules, and classical molecular simulations typically work with ions that do not form chemical bonds, such as alkali metal cations or halide anions.

After introducing the basic terminology, thermodynamic relations, and common conventions (Section 2), we will briefly review the most important experimental sources of information on the structure, dynamics, and thermodynamics of ions in gas and aqueous phases (Section 3). To set the essential background for the following discussion of computational methods, we will consider the justification and criticisms of several ETAs that are most often used as references for microscopic modeling (Section 4). Subsequently we discuss recent quantum and classical computational studies of ion hydration and analyze factors that can negatively

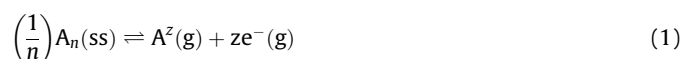
impact their accuracy (Section 5). Finally, we summarize the current status of the subject and outline possible future developments that should lead to better understanding of ion hydration thermodynamics.

2. Thermodynamics of ion formation and hydration

The formation of ions in the bulk aqueous phase can be described by a thermodynamic cycle shown in Fig. 1. In the first major step a gaseous ion is formed from elements in their standard states, and in the second the ion is immersed in pure water. Throughout this manuscript we follow the standard state definitions, conventions, and units used in the NBS compilation of thermodynamic properties [15]. The standard state of pure substances is defined at the temperature of 298.15 K and the pressure of 100 kPa; the standard state of individual ions in aqueous solutions is defined at the temperature of 298.15 K and the concentration of 1 mol per 1 kg of water in the state of an ideal solution; the electron is treated classically and the units follow the SI conventions. The NBS tables also serve as our reference for reliable thermodynamic properties of formation.

2.1. Gas-phase ionization

The formation of gas phase atomic ions can be described by the following reaction



where $A(ss)$ denotes the element A in its standard state, z is the formal charge of the atomic ion, $e^-(g)$ denotes an electron in the gas phase, and n is the number of atoms in the standard state form of element A , e.g., for $H_2(g)$ $n=2$ and for $Na(cr)$ $n=1$. Note that z is negative for anions. The enthalpy of Reaction (1) is given as

$$\Delta_r H^\circ = \Delta_r H^\circ [A^z(g)] + z\Delta_r H^\circ [e^-(g)] - \Delta_r H^\circ \frac{[A_n(ss)]}{n} \quad (2)$$

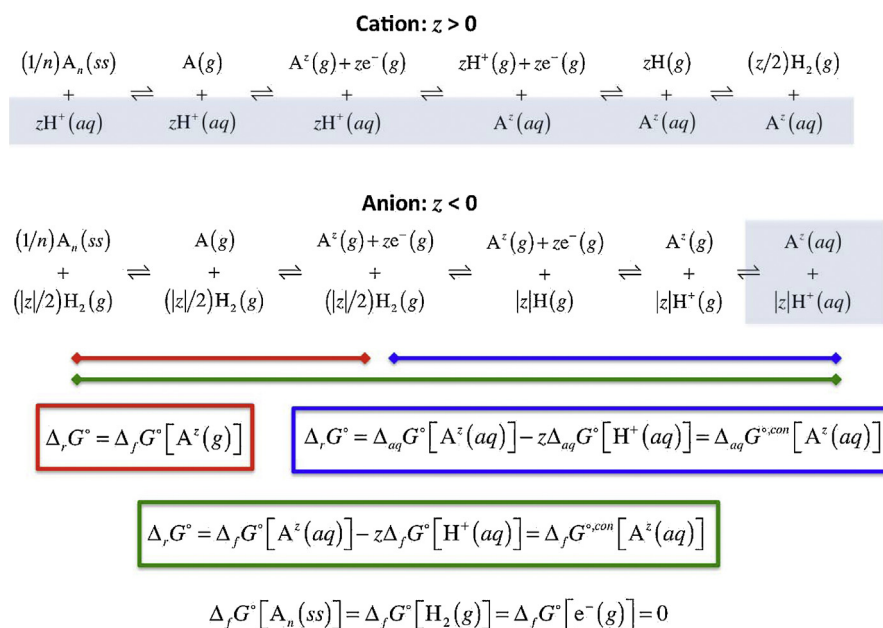


Fig. 1. The thermodynamic cycle of ion hydration following the conventions used in the NBS compilation [15]. Shaded areas denote species in solution with the standard state of 1 mol/kg of solvent. The horizontal lines span reactions and reaction free energies, $\Delta_r G^\circ$, corresponding to the formation of ions in the gas phase (red), hydration of ions (blue), and formation of ions in bulk water (green). Note that the formal charge, z , is negative for anions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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